RAPID CLEAVAGE OF DIARYL ETHERS IN FUEL PROCESSING INDUCED BY ortho-BENZYLIC RADICAL FORMATION: KINETICS OF REARRANGEMENT OF THE 2-PHENOXYBENZYL RADICAL

James A. Franz, John C. Linehan, Anne E. Crump, Lauren Kaune, Mikhail S. Alnajjar,
Donald M. Camaioni, and Tom Autrey

Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99352

INTRODUCTION

Recently we reported the cleavage of the aryl ether bond of 2-benzyldiphenyl ether in reactions with an iron sulfide nanocatalyst in dihydrophenanthrene at 400 °C (1). In that work, the rearrangement of 2-benzyldiphenylether to 2-(diphenylmethyl)phenol and the subsequent rapid scission of 2-diphenylmethylphenol to give diphenylmethane and phenol (eq.1, X = H) was found to occur not

$$X = H, p\text{-}CH_3$$
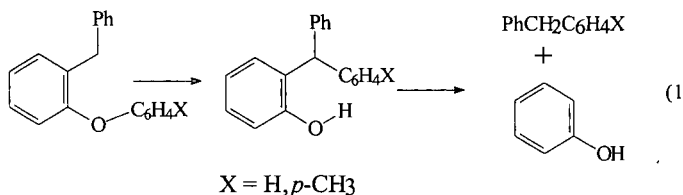
by a direct ether C-O bond scission pathway, but rather by stepwise formation of a benzylic radical followed by phenyl migration from oxygen to the carbon radical center (Scheme 1). Substitution of a methyl group on the phenyl ether ring confirmed that diphenylmethane was formed in a rearrangement reaction (eq 1, X = $p\text{-}CH_3$). Thus, alkyl substituents adjacent to aromatic ether linkages provide a pathway for enhanced thermal cleavage of the relatively inert ether C-O bond. Note that the alternate pathway to eq. 1 is cleavage of the benzyl group to form a diphenyl ether. As shown by the first two entries in Table 1, direct benzyl cleavage is the slow, but favored pathway for the 4-benzyl-substituted diphenylethers. To further explore and quantitate this pathway for strong bond scission in fuels processing, we have determined rate constants for the rearrangement of the 2-phenoxybenzyl radical to the 2-benzylphenoxy radical. We present global rate constants for conversion of substituted diphenyl ethers by nanophase FeS catalysts that illustrate that *ortho* alkyl substitution of a diaryl ether leads to an enhanced rate of scission of the aryl ether bond under hydrocarbon processing conditions.

EXPERIMENTAL

Kinetics of Rearrangement of the 2-Phenoxybenzyl Radical. 2-Phenoxybenzyl radical (**2**, Scheme 1) was formed either by the reaction of 2-phenoxybenzyl chloride and Bu_3SnH or by the photolysis of ketone **1**, Scheme 1, which was prepared by the method of Sasaki and Kitagawa(2). The rearrangement kinetics were performed by photolysis of reagents sealed in quartz tubes in a specially modified GC oven equipped with a quartz photolysis window. The tubes were placed in an aluminum block in the GC oven at reaction temperature through a hole on top of the oven and allowed to equilibrate for 5 minutes prior to photolysis. Solutions containing the ketone 1 (10^{-2} M), tributyltin hydride (1×10^{-4} to 5×10^{-3} M), and eicosane (an internal GC standard) in dodecane were made up in an inert atmosphere box. The solutions were syringed in 100 ul portions into 4 mm o.d. quartz tubes. The tubes were placed on a vacuum line and degassed in three freeze-pump-thaw cycles prior to sealing. Analysis by GC of tubes sealed in this manner showed no evidence of reaction during preparation and sealing. The samples were photolyzed, through a quartz window in the GC oven door, with a 150-watt deuterium/mercury lamp. The reactions were run between 190°C and 270°C to 20% or less consumption of Bu_3SnH. GC analyses were performed on a J&W Scientific 15-m DB-5 column using a Hewlett-Packard model 5890 GC with FID detection. The rate constants were calculated by computer solution of the integrated rate expression relating unrearranged product (**4**), rearranged product (**5**), initial tributyl tin hydride concentration (B_0), and the relative rate $r = k_{re}/k_{abs}$:

$$[4 + 5] = (B_0 + r)*(1-\exp(-[5]/r)) \tag{2}$$

The relative rate constants (r) were combined with an absolute rate expression for abstraction of hydrogen from Bu_3SnH by benzyl radical (3): $log(k_{abs}/M^{-1}s^{-1}) = 8.65 - 5.58/\theta$, $\theta = 2.3RT$ kcal/mol, to yield the rearrangement rate constants k_{re}.

Kinetics of Reactions of Diaryl Ethers With FeS Catalysts. Samples of diaryl ethers (15-20 mg) were sealed in glass ampules in the presence of dihydrophenanthrene (100 mg), FeS catalyst precursor (3 mg), and sulfur (3 mg), and heated in a fluidized sand bath at 390°C. Products were analyzed by GC using authentic products. Detailed procedures for FeS/substrate reactions have been published (4-6).

RESULTS AND DISCUSSION

The 1,4-aryl migration of 2-phenoxybenzyl radical, **2**, to form the 2-benzylphenoxy radical, **3**, follows the Arrhenius rate expression $log(k_{re}/s^{-1}) = (10.8 \pm .8) - (20.2 \pm 1.8)/\theta$, $\theta = 2.3$ RT kcal/mol. These Arrhenius parameters suggest that the rearrangement occurs efficiently at coal liquefaction temperatures ($k_{re} = 3 \times 10^4$ s^{-1} at 700K). The controlling factor for this category of rearrangement will be the efficiency of radical formation and the unimolecular lifetime of the radical relative to bimolecular reaction with available hydrogen donors. With efficient radical initiation, such as in the presence of sulfur-derived thiyl radicals, regeneration of benzylic radicals will occur through many cycles. Once the radical has undergone rearrangement, subsequent trapping by available hydrogen donors produces an ortho-hydroxydiphenylmethane, which undergoes rapid unimolecular homolysis (7).

Rate constants for the disappearance of methyl substituted 2- and 4-benzyldiphenylethers (Table 1) reveal that benzyl substitution at the 2-position enhances the rate of "uncatalyzed" ether conversion by a factor of 30 compared to substitution at the 4-position. For the catalyzed cases, the 2-benzyl-substituted diphenyl ether is about 10 times more reactive than the 4-benzyl-substituted diphenyl ether. Table 1 shows that for the cases of 4-benzyl-substituted diphenylmethanes, catalyzed cleavage of the benzyl-aromatic ring C-C bond occurs exclusively, illustrating the regiochemical requirements for C-O cleavage leading to diphenylmethane formation. These results demonstrate a pattern of enhancement of cleavage of diaryl ethers consistent with the participation of the 1,4- oxygen-to-carbon aryl migration reaction.

ACKNOWLEDGMENT

REFERENCES

(1) Autrey, T.; Linehan, J.C.; Camaioni, D. M.; Powers, T. R.; McMillan, E. F. And Franz, J. A. *Fuel Preprints*, **1995**, 973-977.

(2) Sasaki, H. And Kitagawa, T. *Chem. Pharm. Bull.* **1983**, 31, 2868.

(3) Franz, J.A.; Suleman, N.K.; and Alnajjar, M.S. *J. Org. Chem.* **1986**, *51*, 19-25.

(4) Autrey, T.; Linehan, J.C.; Camaioni, D.M.; Kaune, L.E.; Watrob, H.M.; and Franz, J.A *Catalysis Today*, **1996** *31* , 105-111.

(5) Matson, D.W., J.C. Linehan, J.G. Darab, D.C. Camaioni, S.T. Autrey, and E. Lui. **1995**, "New Nanopohase Iron-Based Catalysts for Hydrocracking Applications" MRS Symposium Proceedings #368, Synthesis and Properties of Advanced Catalytic Materials, E. Iglesia, P.W. Lednor, D.A. Nagaki, L.T. Thompson, eds. pp.243-248.

(6)Linehan, J. C.; Matson, D. W.; and Darab, J. G. *Energy & Fuels* **1994**, 56.

(7) McMillen,D.F; Ogier, W. C.; and Ross, D. S. *J. Org. Chem.* **1981**, 46, 3322.

Table I
Rate Constants for the Disappearance of Benzyldiphenyl Ethers
with Iron-Sulfide Catalysts

Substrate[a] DPM/DPE	Catalyst Precursor[b]	Rxn Temp	$k \, (1 \times 10^4 s^{-1})$	% Consumed[c]
(4'Me)-4-BzDPE	none	390°C	0.04 ± .005	3	d
(4'Me)-4-BzDPE	6-line	390°C	0.40 ± .08	25	0.02[e]
(4'Me)-2-BzDPE	none	390°C	1.3 ± .2	50	70[f]
(4'Me)-2-BzDPE	6-line	390°C	3.8 + .3	90	23[f]

a) DPM = diphenylmethane, DPE = diphenylether, 4-BzDPE = 4-benzyldiphenylether, 2-BzDPE = 2-benzyldiphenylether, (4'Me)-2-BzDPE = 4'-methyl-2-benzyldiphenylether, (4'Me)-4-BzDPE = 4'-methyl-4-diphenylether. b) 6-line = 6-line ferrihydrite, see refs. 4-6. c) Percent consumed in 90 minutes. d) No DPM observed. e) MeDPM/MeDPE. f) 4-methyldiphenyl -methane and 4-methyldiphenylether.
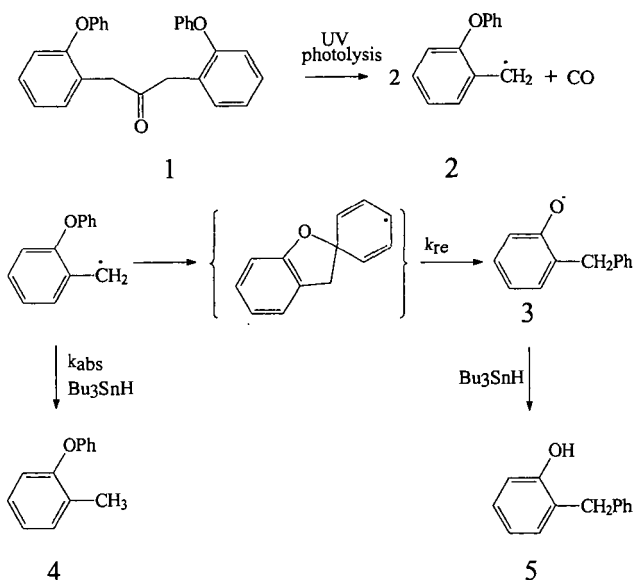
Scheme 1. Photolysis of Ketone 1 provides radical 2, which undergoes irreversible rearrangement, k_{re}, in competition with hydrogen abstraction, k_{abs}, from Bu_3SnH.